Electrical Transport Properties of Polycrystalline Chromium Vanadate

Shubha Gupta, Y. P. Yadava, and R. A. Singh
Department of Physics, University of Gorakhpur, Gorakhpur 273009, India

Z. Naturforsch. **42a,** 577–581 (1987); received February 3, 1987

Electrical transport properties of polycrystalline chromium vanadate ($CrVO_4$) have been studied by measuring its a.c. and d.c. electrical conductivities, thermoelectric power and dielectric constant in the temperature range 300–1000 K. $CrVO_4$ is a p-type semiconductor with an energy gap of 3.6 eV. The compound exhibits extrinsic nature up to $T \sim 750$ K and after that its intrinsic nature arises. The activation energy and charge carrier mobility in the temperature ranges 300–750 K and 750–1000 K show that the conduction in the extrinsic region is due to a small polaron hopping mechanism and in the intrinsic region it is of the normal band type.

1. Introduction

In the present paper, an attempt has been made to explain the conduction mechanism in $CrVO_4$ in its normal orthorhombic form [1]. Six oxygen atoms surround each chromium atom and form a somewhat distorted octahedron. Four oxygen atoms group around each vanadium atom and form a nearly regular tetrahedron. Its crystallographic and thermodynamic properties have been studied by various workers [2, 3]. Its melting point is 1083 K [3].

The magnetic properties of $CrVO_4$, i.e. its electron paramagnetic resonance [4], magnetic susceptibility [5] and magnetic resonance of the ^{51}V nuclei [6] reveal that it is an antiferromagnetic compound with the Neel temperature 51 ± 1 K [2, 4].

This paper reports on measurements of the a.c. and d.c. electrical conductivities, thermoelectric power and dielectric constant in the temperature range 300–1000 K. The data thus obtained are analyzed to explain the conduction mechanism in $CrVO_4$.

2. Experimental

Polycrystalline $CrVO_4$ was procured from M/S Rare and Research Chemicals, Bombay, India (nominal purity 99.99%). Since pellets become almost independent of pressure at 5×10^6 g/cm², a pellet of 1.82 cm diameter and 0.18 cm thickness was made applying a pressure of 6×10^6 g/cm². For annealing the pellet was kept in a tightly closed platinum crucible at 800 K for 24 h. Then both faces of the pellet were painted with silver paint procured from the National Physical Laboratory, New Delhi. The pellet was placed between two platinum electrodes in a stainless steel sample holder. For electrical and thermal insulation purposes, mica sheet was used.

The d.c. electrical conductivity was measured with a digital multimeter (PM 2522/90, Philips, India) with an accuracy better than ±0.25%. The a.c. electrical conductivity and dielectric constant were measured with a Universal LCR Bridge, model 901-I Ruttonsha Simpson (India), which operates at an internal frequency of 1 kHz with an accuracy of ± 1.25% of the reading, ±0.25% at full scale range. The dielectric constant of the sample was determined at various temperatures by measuring the capacity of the parallel plate capacitor with the pellet as dielectric medium.

For the measurement of the thermoelectric power of the sample, a microfurnace was placed just below one of the platinum electrodes and a temperature difference of ~20 °C was produced. Chromel-alumel thermocouples were firmly attached to the platinum electrodes. Each reading was taken after attainment of thermal equilibrium (about 2½ h). The details of the apparatus and measuring procedure have been described by Bharati et al. [7].

Reprint requests to Dr. R. A. Singh, Department of Physics, University of Gorakhpur, Gorakhpur 273009, India.

0932-0784 / 87 / 0600-0577 $ 01.30/0. – Please order a reprint rather than making your own copy.

3. Results

The logarithms of the a.c. and d.c. electrical conductivities ($\log \sigma_{\text{a.c.}}$ and $\log \sigma_{\text{d.c.}}$) vs. the inverse temperature ($10^3/T$) are plotted in the Figure 1. A marked kink occurs at $T \sim 750$ K. In the temperature range 300–750 K, the a.c. conductivity is larger than d.c. conductivity, but for $T \sim 750$ K the two conductivities become almost equal. Using the relation

$$\sigma = \sigma_0 \exp\{-W/kT\} \tag{1}$$

with k in units eV/K, the observed temperature dependence of $\sigma_{\text{d.c.}}$ yields

$$\begin{aligned} \sigma_0 &= 4.4 \times 10^{-4}\ \text{ohm}^{-1}\,\text{cm}^{-1} \quad \text{and} \\ W &= 0.34\ \text{eV} \quad \text{for} \quad 300 \leqq T \leqq 750\ \text{K}, \end{aligned} \tag{2}$$

and

$$\begin{aligned} \sigma_0 &= 1.99 \times 10^{7}\ \text{ohm}^{-1}\,\text{cm}^{-1} \quad \text{and} \\ W &= 1.83\ \text{eV} \quad \text{for} \quad 750 \leqq T \leqq 1000\ \text{K}. \end{aligned} \tag{3}$$

For the measurement of the thermoelectric power (S), the formula used is

$$S = \Delta E/\Delta T, \tag{4}$$

where ΔE is the thermo e.m.f. produced across the pellet due to the temperature difference ΔT. The thermoelectric power of $CrVO_4$ was measured in the temperature range 300–1000 K, and ΔT was kept at approximately 20 K. A plot of S vs. $10^3/T$ is shown in Figure 2. Its positive value in the entire temperature range shows that $CrVO_4$ is a p-type semiconductor with holes as majority charge carriers. The variation of S in units V/K with T according to the simple two band model is given by [8]

$$S = \eta/T + K, \tag{5}$$

where

$$\eta = -\frac{W}{e}\left(\frac{c-1}{c+1}\right), \tag{6}$$

$$K = -\left[\frac{2k}{e}\left(\frac{c-1}{c+1}\right) + \frac{3k}{4e}\ln a\right], \tag{7}$$

$$c = \mu_e/\mu_h \quad \text{and} \quad a = m_e/m_h\,.$$

Here m_e, μ_e and m_h, μ_h are effective masses and mobilities of electrons and holes, respectively. The charge carrier mobility has been calculated from (2), (3) and (5) together with the value of σ_0 given by

$$\sigma_0 = 2e\left(\frac{2\pi kT}{h^2}\right)^{3/2} (m_e m_h)^{3/4} (\mu_e + \mu_h), \tag{8}$$

where T is the mean temperature of the respective range. The charge carrier mobility comes out, to be 2.7×10^{-4} and $11.6\ \text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ in the temperature ranges 300–750 K and 750–1000 K, respectively.

The dielectric constant at various temperature has been estimated using the formula [9]

$$\varepsilon' = c\,\frac{11.3\,t}{A}, \tag{9}$$

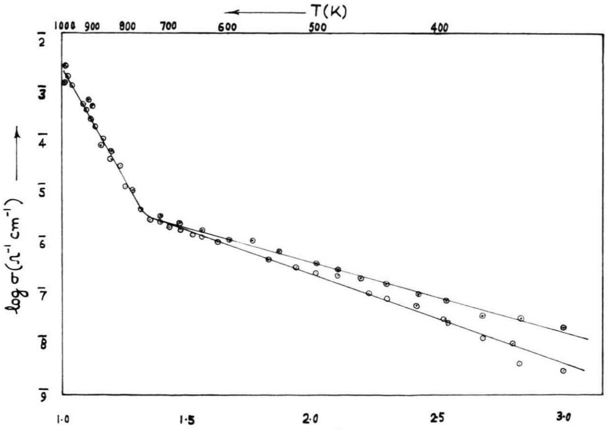

Fig. 1. $\log \sigma_{\text{a.c.}}$ and $\log \sigma_{\text{d.c.}}$ vs. $10^3/T$. ⊗: a.c. conductivity, ⊙: d.c. conductivity.

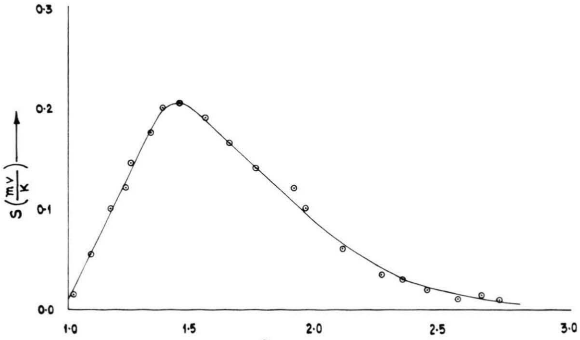

Fig. 2. Variation of thermoelectric power (S) with $10^3/T$.

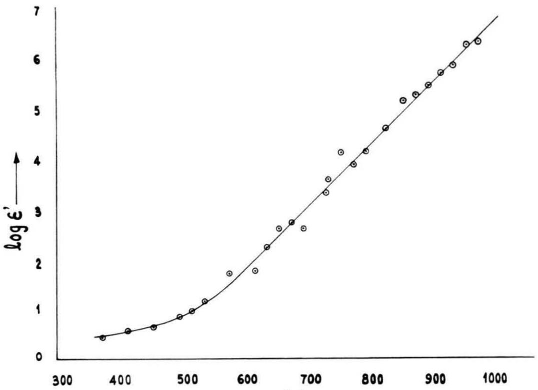

Fig. 3. Variation of log ε' with T.

where ε' is the dielectric constant, c the capacitance in picofarads, t the thickness of the pellet in centimeters and A the area of the electrode in square centimeters. A plot of log ε' thus obtained vs. T is shown in Figure 3.

4. Discussion

To understand the electrical conduction in 3d-transition metal compounds, the 3d-states must be included explicitly. They are described by narrow bands, which lie between the top of the valence band, represented by the filled 2p states of the oxygen, and the bottom of the conduction band, which is described by 4s and 4p states of the transition metal elements [10]. These conduction bands have in addition 3d character too. The d-states are partially filled in this compound, the electronic states being $3d^3$ for Cr^{3+} and 3d for V^{5+}. There is a strong crystal field splitting due to the ionic nature [11] of the nearest neighbour cluster of the O^{2-} ions. It splits the d-states into a lower t_{2g} and an upper e_g set of states [12]. This picture has been verified from X-ray experiments for Cr_2O_3 [13]. Therefore there are occupied narrow 3d bands of t_{2g} nature as well as unoccupied ones of t_{2g} and e_g nature for both ions within the band gap.

The probable conduction mechanisms which are responsible for the electrical conduction in $CrVO_4$ are as follows:

(i) By exciting an electron from the filled valence band to the empty conduction band and thereby forming an electron-hole pair.

(ii) By transferring an electron from the O^{2-}: 2p band to the chromium 3d bands, thus creating a hole in the O^{2-}: 2p band.

(iii) By transferring an electron from a filled narrow sub-band to an empty narrow sub-band of Cr^{3+}, thus forming a hole in a filled narrow sub-band.

(iv) By Cr^{4+} ions, present as a result of native defects, which are often present in 3d-transition metal oxides.

For the formation of an electron-hole pair, the activation energy should be of the order of 2.3 eV. Such a value has been obtained for Cr_2O_3 [13]. For the conduction mechanisms (ii) and (iii), the activation energy should be about 1 eV (because the crystal field splitting 10 Dq is approximately 2 eV [10].

In the low temperature region (300 – 750 K), the activation energy is 0.34 eV, which is too low to be the activation energy for intrinsic conduction. So, it may be associated with some sort of impurities and defects. Since Cr_2O_3 is an oxygen excess semiconducting oxide [14 – 16] which leads to the formation of Cr^{4+} ions, it is concluded that $CrVO_4$ contains Cr^{4+} ions as impurities.

The charge carrier mobility in the low temperature region has been estimated as 2.7×10^{-4} cm^2 V^{-1} s^{-1}. The low value of the charge carrier mobility and the activation energy indicate that small polaron conduction takes place in this compound. The formation of small polarons seems to be quite probable due to the presence of narrow 3d-bands and due to the ionic nature of $CrVO_4$. Small polarons conduct either via a hopping mechanism or by a band mechanism. In the temperature region 300 – 750 K, small polaron band conduction cannot take place [17]. Therefore the only possibility left is conduction via a small polaron hopping mechanism in which the charge carrier mobility increases exponentially with temperature. In this compound, the charge carrier mobility increases with temperature as evidenced by the increase in the thermo-electric power with temperature below 750 K. It is concluded that the conduction in the low temperature region is due to transfer of small polarons from the ions of chromium in different valence states, e. g. $Cr^{3+} \rightarrow Cr^{4+}$. The increase in the conductivity is mainly due to an increase in the charge carrier mobility because in the extrinsic region the number of the charge carriers becomes constant above some temperature.

In the case of small polaron hopping conduction, the electrical conductivity σ follows the relation [18]

$$\sigma T^{1/2} = A(T) \exp\{-E_h/kT\}, \qquad (10)$$

where $A(T)$ is almost constant and E_h is the small polaron hopping energy. When this function is fitted to the experimental curve instead of the original function ((1), Fig. 1), the value of E_h comes out to be 0.24 eV. The hopping energy 0.24 eV obtained this way is smaller than the original activation energy 0.34 eV below 750 K. The difference is interpreted as the polaron binding energy. Therefore, in this compound small polaron hopping conduction is confirmed in the extrinsic region.

In the temperature range 750–1000 K, the activation energy found is 1.83 eV. This leads to a band gap of 3.6 eV. Badwal and Bevan [19] have also measured the electrical conductivity and have reported the activation energies as 0.91 eV and 0.57 eV in the temperature ranges 735–880 K and 880–1030 K, respectively. The difference between the activation energy (1.83 eV) estimated by us and the activation energies 0.91 and 0.57 eV estimated by Badwal and Bevan may be due to the following reason: Initially the presence of impurities and grain boundaries etc. affect the electrical conductivity to a larger extent. Badwal and Bevan have measured the electrical conductivity of the pressed pellet of $CrVO_4$ from 735–1030 K. It seems that impurities and grain boundaries etc. are not completely removed, and they are affecting the electric conductivity to a considerable extent. So the activation energy estimated by them may not be taken as the activation energy for intrinsic conduction. We have measured the electrical conductivity from 300 K, and by the time the temperature reaches to 750 K the impurities, defects, water molecules etc. get eliminated and the intrinsic conduction sets on. Hence the activation energy 1.83 eV estimated by us represents the intrinsic activation energy.

The activation energy 1.83 eV is too high for the conduction mechanisms (ii) and (iii) to take place because for these conduction mechanisms the activation energy should be of the order of 1 eV. Therefore it is concluded that mechanism (i) dominates in the region 750–1000 K. The charge carrier mobility there is 11.6 $cm^2\,V^{-1}\,s^{-1}$ and the mean free path (L), which has been estimated using the expression [20]

$$L = \frac{3\mu}{4e}\sqrt{2\pi k T m_h}, \qquad (11)$$

is 45.83 Å. Higher values of the charge carrier mobility and the mean free path and a decrease in the mobility with temperature (as clear from the decrease in thermoelectric power with temperature) [21] confirm that in this temperature range the conduction is of the normal band type.

The change at $T \sim 750$ K in the thermoelectric power vs. temperature plot is associated with the change in the conduction mechanism from extrinsic to intrinsic. The increase in thermoelectric power with temperature up to 750 K is due to the small polaron hopping mechanism because in this mechanism the mobility of the charge carriers increases. The decrease in thermo-electric power with temperature in the range 750–1000 K confirms that the electrical conduction in this range is of the normal band type. In normal band type conduction, the decrease in the thermoelectric power is due to the exponential increase in the number of charge carriers and the decrease in the mobility of the charge carriers.

The slow variation of the dielectric constant with temperature is due to the ionic nature of the compound [22]. At low temperature and low frequency, all the four factors, i. e. ionic, electronic, dipolar and space charge polarization contribute to the dielectric constant. Since we have measured the dielectric constant at the relatively low frequency of 1 kHz, all these factors will contribute to ε' in the temperature range 300–750 K. With increasing temperature, the lattice of the crystal expands with a consequent increase in the polarizability of the ions.

Above 750 K, the rapid increase in ε' with temperature is due to the intrinsic nature of the compound. In the intrinsic semiconductor, the number of charge carriers increases exponentially with increasing temperature, which increases the dielectric constant to a larger extent.

Acknowledgement

The authors are grateful to the Department of Science and Technology, Government of India, New Delhi, for financial assistance.

[1] K. Brandt, Ark. Kemi, Min Geol. **A17**, 6 (1943).
[2] B. C. Frazer and P. J. Brown, Phys. Rev. **125**, 1283 (1962).
[3] A. S. Borukhovich, I. I. Miller, M. S. Marunya, and A. A. Fotiev, Inorg. Mater. (USA) **11**, 830–831 (1975).
[4] P. R. Elliston, Canad. J. Phys. **47**, 1865–1868 (1969).
[5] V. I. Surikov, I. I. Miller, V. I. Surikov, V. N. Lission, L. A. Vgognikova, and E. M. Yarosh, Sov. Phys. Solid State (USA) **21**, 913 (1979).
[6] R. N. Pietner, V. N. Lission, and V. A. Gubanov, Sov. Phys. Solid State (USA) **15**, 336 (1973).
[7] R. Bharati, R. A. Singh, and B. M. Wanklyn, J. Phys. Chem. Solids **43**, 641 (1982).
[8] T. C. Herman and J. M. Honing, Thermoelectric Power and Thermomagnetic Effects and Applications, McGraw Hill, New York 1976.
[9] J. P. Suchet, Electrical Conduction in Solid Materials, Pergamon Press, Oxford 1975.
[10] B. H. Brandow, Adv. Phys. **26**, 651 (1977).
[11] K. Hubner, Phys. Stat. Solidi (b), **69**, K1 (1975).
[12] D. Adler, Rev. Mod. Phys. **40**, 193 (1968).
[13] D. W. Fischer, J. Phys. Chem. Solids **32**, 2455 (1971).
[14] D. de Cogan and G. A. Longergan, J. Phys. Chem. Solids **38**, 333 (1977).
[15] W. C. Hagel, J. Appl. Phys. **36**, 2586 (1965).
[16] J. A. Crawford and R. W. Vest, J. Appl. Phys. **35**, 2413 (1964).
[17] I. K. Naik and T. Y. Tien, J. Phys. Chem. Solids **39**, 311 (1978).
[18] I. G. Austin and N. F. Mott, Adv. Phys. **18**, 41 (1969).
[19] S. P. S. Badwal and D. J. M. Bevan, J. Aust. Ceram. Soc. **15**, 28 (1979).
[20] M. Przybylski, A. Graja, A. Rajchel, M. Gawron, and T. Borowiak, Commun. to Phys. Stat. Solidi (a).
[21] S. Methfessel and D. C. Mattis, Handbuch der Physik XVIII/I, edited by S. Flugge, Springer-Verlag, Heidelberg 1968.
[22] C. P. Smyth, Dielectric Behaviour and Structure, McGraw Hill, New York 1955.